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January 1, 1984 to June 30, 1984

SUPERCONDUCTING ELECTRONIC FILM
STRUCTURES

By

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Solid state epitaxial growth of NbN single crystals have now been achieved on (1, -1, 0, 2) sapphire. Results indicate that surface preparation is the most critical factor in obtaining epitaxy. Films of V-Si and Nb-Ge have been reactively magnetron sputtered and the A15 phase has been obtained at temperatures as low as 290°C, approximately 150°C lower than with dc diode reactive sputtering. A LEED study of Nb_3Ir single crystal epitaxial substrates lead to in-situ surface processing procedure and showed that surface reconstruction is caused by oxygen impurity. Epitaxial, single crystal Nb films have been prepared on sapphire and MgO substrates. A glancing angle XPS study of Al_2O_3 tunnel barriers and extremely thin amorphous Mo-Ge films demonstrated universality of significant thickness variation that affects tunnelling characteristics.

3. OBJECTIVES

The objectives of the Westinghouse-AFOSR program are:

1. Investigate the low-temperature synthesis of high-critical-temperature superconducting films.

2. Grow epitaxially single-crystal superconducting films and coherent layered structures.

3. Characterize the near-surface crystalline perfection of superconducting layers and their interfaces by in situ methods.

4. Study tunnelling into high-critical-temperature superconducting films and other electronic film properties.

5. Explore electric characteristics of layered film structures.

4. ACCOMPLISHMENTS

4.1 Preamble

This research program was initiated in January 1983. The research is aimed at understanding and improving superconducting and normal state properties of layered, epitaxial thin film structures incorporating high-critical-temperature superconductors. Anticipated results will form a material science base for future technology of high-operating-temperature superconducting electronics. Successful completion of certain portions of this program required the purchase and installation of a new type of deposition and in situ analytical facility hereafter termed as the Superlattice Facility (SF). This facility was delivered by Riber S. A. of France in the latter part of 1983. Its installation is now completed and testing is proceeding along with experimental work. Details of work involving this new facility and other accomplishments of the program are presented below.

4.2 Low-Temperature Synthesis of High-T_c Films

Low-temperature synthesis of high-T_c superconducting films is required for S-I-S tunnel junction fabrication to avoid barrier damage. It is also of considerable scientific interest to further the understanding of the kinetics of stable and metastable A15 compound formation, and especially of the "stabilization effects." At present, with the new SF almost completely operational, the work on impurity-controlled low-temperature reactions between A and B elements to form A_3B superconducting A15-structure compounds is finally progressing as originally planned. The Nb-Sn diffusion couples and Nb_3Sn films synthesized with controlled amounts of oxygen impurity represent the first object of this investigation. Ultra-pure niobium single crystals (less than 10 ppm of interstitials) were especially prepared for this study by Max Planck Institute in Stuttgart, West Germany. Very thin Nb_3Sn films having T_c onsets of ~ 17K have already been obtained in ultra-high-vacuum of low 10^{-10} torr at temperatures well below 700°C. This work is, however, in an initial stage, and will have to continue into the following years to produce in-depth scientific and technological results.

As reported in 1983 Annual Report for this program, a major advance in the low-temperature synthesis of A15 compounds was accomplished by investigating the reactive sputtering of V_3Si and Nb_3Ge using, respectively, silane and germane. It follows from the consideration of the silane and germane reactivity that this method would be particularly promising for low-temperature synthesis. Tunnel barrier formation by low-temperature, low-pressure chemical vapor deposition (CVD) of Si and Ge is compatible with the method and also of considerable technological interest. Previously, Nb_3Ge could not be obtained reproducibly by reactive sputtering, and very little was known about the reactive sputtering of V_3Si. The film depositions were performed in a phase spread configuration obtained by locating the reactive gas inlet asymetrically with respect to the substrate holder. Using a dc diode sputtering process with a small cathode-anode distance, a normalized cutoff temperature was discovered below which no x-ray identifiable structure with a $T_c > 4.2K$ could be obtained. For A15's that temperature was found to be higher than 400°C. The effect was attributed to structural damage by energetic particles bombarding the film being deposited in the dc diode closed-spaced configuration.

During this reporting period, films were reactively sputtered in a magnetron system having a large cathode-anode separation. Although the new SF includes a UHV magnetron sputtering capability, a second much simpler magnetron system was used for these experiments. The reactive sputtering of V_3Si and Nb_3Ge requires the use of SiH_4 and GeH_4 gas and a background impurity level of the order of 10^{-6} torr. Since the introduction of this type of contamination into the SF was deemed unadvisable at this time, this second magnetron system was constructed (at no cost to AFOSR). This system has a single U. S. Gun I sputtering head, a high-temperature substrate heater, and a mixing chamber for preparing the desired GeH_4/Argon and SiH_4/Argon mixtures. The system uses diffusion pumping and has a background impurity level in the low 10^{-6} torr region. Using magnetron sputtering V-Si and Nb-Ge films were prepared which were found to be dramatically different from those deposited in the dc diode system. V_3Si films prepared in the magnetron system crystallized into the A15 structure at deposition temperature as low as 290°C compared to the previous minimum temperature of ~ 450°C. These films were superconducting with T_c's of ~ 7K. A second significant observation was that the dependence of resistively measured critical temperature on film composition was very different. In the case of the V-Si films that were dc diode sputtered, near optimum T_c's of ~ 16K were found in films having average compositions ranging from $V_{83}Si_{17}$ to $V_{64}Si_{36}$. Studies on bulk samples have shown that such high critical temperatures are obtained in the V-Si system only at compositions at or very near to $V_{75}Si_{25}$. It is believed therefore that these high T_c's must be due to regions of films having 3/1 stoichiometry which are incorporated in a matrix of non-3/1 stoichiometric material. The validity of this conjecture is now being investigated using scanning transmission electron microscopy. A distinctly different dependence of critical temperature on composition was found in the magnetron sputtered films. In this case T_c peaked in films having 3/1 stoichiometry and dropped sharply on either side of this composition. A more detailed discussion of all these results will be included in a paper which has been accepted for presentation at the 1984 Applied Superconductivity Conference.

4.3 Epitaxial Growth of Superconducting Films

The investigation of epitaxial growth processes leading to the formation of single crystal A15 and B1-structure films has a technological as well as a scientific motivation. Elimination of near-interface structural disorder in layered film structures will make high-T_c S-I-S tunnel junctions possible. Availability of single crystals of high-T_c superconducting materials will permit the investigation of their intrinsic properties and will advance the science of superconductivity.

During 1983 work under the present program concentrated on the epitaxial growth of B1-structure niobium nitride, NbN, since this did not require, at least initially, the use of the Superlattice Facility. The first observation of the solid-state epitaxy of NbN on sapphire substrates represented a major achievement of this program. This study has continued during this reporting period. Single crystal NbN films have now been deposited on sapphire with a $(1\bar{1}02)$ as well as the $(2\bar{1}\bar{1}3)$ surface orientation. The present data point toward a conclusion that surface preparation and cleanliness are more important than surface orientation for obtaining epitaxial growth. This tentative conclusion is currently being tested by preparing films on sapphire substrates having a variety of surface orientations and surface treatments.

In all of the films obtained so far there is a structurally correlated network of hole (pores) that might make tunnelling experiments difficult. Initial tunnelling work on these films using native oxide barriers is in progress.

A presentation of initial results on NbN single crystal growth was made at the March 1984 APS Meeting. A paper which also includes more recent data has been accepted for presentation at the 1984 LT-17 Conference and will be published in the proceedings of that conference.

Work on epitaxial A15 films is centering on Nb_3Ge since single crystals of Nb_3Ir for epi-substrates were obtained at no major cost to the program. The Nb_3Ir should be an ideal epitaxial substrate material because of its A15 structure and lattice parameter similar to that of Nb_3Ge. Two single-crystal Nb_3Ir rods, 6 mm in diameter and with (100) major axis, were prepared in 1983 for use in this program through the courtesy of Dr. Eric Walker, using the crystal growing and zone refining facilities at the University of Geneva in Switzerland. Raw materials for the synthesis were supplied by this program.

During this reporting period, extensive characterization of the Nb_3Ir rods was done using x-rays, electron microprobe, and electron diffraction. These appear to be the first high-quality Nb_3Ir crystals ever grown. A method for, epitaxial Nb_3Ir substrate preparation has been developed based on XPS characterization, reflection electron diffraction (RHEED), and especially low energy electron diffraction (LEED). The LEED technique permitted one to determine in-situ substrate processing conditions that for (100) substrates result in a perfect 1 x 1 diffraction pattern representing the top few atomic monolayers. Surface reconstruction effects have also been observed by LEED and attributed to the injection of oxygen impurity. These effects, essential for understanding the nucleation stage of epitaxial growth, will be studied in more detail.

An activity parallel to that described above has been initiated with yttria-doped ZrO_2 substrate crystals. These crystals have a lattice parameter compatible with Nb_3Ge but a different crystal structure (that of calcium fluoride). The x-ray characterization and orientation is completed and substrates of various orientations are being fabricated.

The growth of Nb_3Ge is in progress using the magnetron sputtering chamber of the Superlattice Facility. High-T_c polycrystalline Nb_3Ge has already been obtained. Epitaxial growth experiments using Nb_3Ir and ZrO_2 substrates are scheduled to begin in the second half of 1984 and to continue in 1985.

To complement the study of epitaxial B1 and A15 layers, single crystal films of niobium have also been fabricated in SF using sapphire and MgO substrates of various orientation. The single-crystalline nature of these atomically-smooth films has been determined by in-situ RHEED. These films will be used in studies described in Section 4.2, in studies of RF surface losses (in collaboration with the MIT-Lincoln Laboratory), and in a spectroscopic $\left(\alpha^2F(\omega)\right)$ study of tunnelling anisotropy.

In addition to the experimental studies that were described above, a computational study is in progress. Existing computer programs to predict and evaluate mutual orientation of calcium phosphate polycrystals are being modified to handle cubic crystals and remove errors. These programs compare or "match" two crystal structures by picking the best matching directions (lowest misfits) for interatomic spacings and angles in two dimensions, and also by generating numerical figures of merit. At present, the programs are being run for known test cases (NbN/Al_2O_3, NbN/MgO, Nb_3Ge/Nb_3Ir and Nb_3Ge/ZrO_2). If effective, the programs will be used to predict the most feasible crystal substrates and the best matching crystal orientations. This could be of use to researchers in other fields.

4.4 Characterization of Near-Surface Layers

The purpose of this task is to apply and develop methods of surface and interface characterization that are appropriate for the in-situ investigation of thin films and layered structures generated under other tasks of the program. Crystallinity, phase composition, and physical uniformity are of particular interest.

The investigation originally planned under this tasks requires using the in-situ analytical equipment of the Superlattice Facility. As in the case of preceding tasks (Sections 4.2 and 4.3), the delay in the delivery and startup of this facility made it impossible to proceed with in-situ investigations until very recently. At present, the in-situ determination of crystallinity by RHEED is routinely being done in the fabrication of films and tunnel junctions in the Superlattice Facility. Attempts to use ~~in~~ in-situ XPS and Auger spectroscopy have also been made. In the reporting period, however, the analytical equipment did not perform satisfactorily. It was eventually aligned and debugged by the vendor's service personnel by the end of June, 1984. The data manipulation software is still being debugged.

In spite of the unsatisfactory performance of the SF surface spectroscopy equipment, a significant accomplishment was made possible in this reporting period through the extensive use of a separate surface analysis facility (VG Escalab Mark II). A mode of experimentation was established to simulate, as far as possible, the in-situ situation, and work concentrated on the tunnel barrier characterization that did not necessarily require to be addressed in-situ.

The physics and technology of tunnel barriers are the least advanced and little understood aspects of the superconducting tunnel junction problem. Further technological progress hinges upon a change in that situation. The barrier studies under this program used niobium base as a reference superconductor in order to temporarily separate the issues pertinent to high-T_c superconductor surfaces from those of barriers. The first task addressed was that of the barrier physical characterization. The x-ray photoelectron spectroscopy (XPS) was for the first time employed to determine the barrier average thickness as a function of the XPS detection angle measured from normal to the film. A theoretical model exists that predicts the thickness to be independent of angle for a flat overlayer of uniform thickness but decrease with increasing angle if the thickness varies. The apparent thickness vs angle dependence for a layer with a Gaussian distribution of thickness characterized by the standard deviation, σ, can be calculated to compare with experiment.

Experimental XPS results were obtained on both Westinghouse and Stanford University ultrathin films and barriers. The smoothest ultrathin films in existence are those of amorphous Mo-Ge, 10 to 25 Å thick, that are studied at Stanford. A thickness variation corresponding to $\sigma > 1$ was, however, found by the new method. For tunnel junction barriers the variation (σ) was much larger still. A consideration of these and similar results, along with the obtained I-V tunnel junction characteristics, lead to the extremely important conclusion that the actual tunnel junction properties are defined by the thinnest and thus most defective regions of the barrier. This is a result universally applicable to all junctions fabricated by various research groups.

Consequently, one of the main directions of work aimed at further improvements in tunnel junction properties must be to study parameters improving barrier thickness uniformity.

A paper describing this work was accepted for presentation at the 1984 Applied Superconductivity Conference.

4.5 Tunnelling

The study of tunnelling into high-T_c superconductor represents a task of direct technological consequence while at the same time providing information about the intrinsic properties of the superconductor near its surface.

Work during 1983 consisted of, first, learning to fabricate and characterize Nb-base tunnel junctions with, mostly, Al/Al_2O_3 barriers. This was the necessary "catch-up" effort to reach the state-of-the-art as established in 1981-1983 at Bell Laboratories. Eventually, junctions with nearly ideal current-voltage (I-V) characteristics for quasiparticle tunnelling have been obtained using Pb-Bi soft alloy counterelectrodes. The fabrication was performed in a UHV chamber equipped with two magnetron guns prior to having it connected to the Superlattice Facility.

In this reporting period, the properties of Nb tunnel junctions having Al barrier layers fabricated by magnetron sputtering, have been compared with those of junctions with barriers e-beam evaporated in the Superlattice Facility. The Nb base electrode films have been deposited in SF at ambient temperature (less than 100°C), and were polycrystalline, as determined by in-situ RHEED. Magnetron sputtered barriers were found to be more uniform.

Work in progress concentrates on tunnelling into high-T_c Nb_3Sn and V_3Si deposited at 800 to 950°C in SF to determine whether the fabrication procedure evolved is applicable to A15 superconductors that, in contrast to Nb, are grown at high temperatures. This work is in progress using XPS as a diagnostic tool.

Work is also in progress on adapting an existing computer program for $\alpha^2F(\omega)$ tunnelling spectroscopy.

4.6 Exploration of Electrical Characteristics of Layered Film Structures

As proposed at the inception of the program, this task is to be addressed in the final phase of the activity. Consequently, no effort was devoted to it. In the proposed continuation of this program the task is reformulated to specifically provide superconducting materials backup for the MIT — Lincoln Laboratory research and development of analog signal processing devices. The RF surface loss (resistance) of various, mostly high-T_c materials will be studied. The first step, presently in progress, is to fabricate in SF various e-beam evaporated niobium films, both polycrystalline and epitaxial for comparison with properties of sputtered Nb films currently fabricated and used by Lincoln Laboratory. This should permit one to determine the effects of crystalline order and purity on RF losses in a reasonably well understood model system.

5. PUBLICATIONS

1. "Pulsed Electron Beam Annealing of A15 Tape Superconductors,"* A. I. Braginski, J. Greggi, M. A. Janocko, T. Kleiser, and O. Meyer, Accepted for publication in Nuclear Instr. and Methods of Phys. Res.

2. "Solid State Epitaxial Growth of Single Crystal NbN on Sapphire," J. R. Gavaler, J. Greggi, and J. Schreurs, Accepted for publication in Proceedings of LT-17 Conference.

*Prepared during the previous contract period, recently revised.

6. PERSONNEL

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J. R. Gavaler }

J. Greggi

M. A. Janocko

J. Schreurs

J. Talvacchio

7. COUPLING ACTIVITIES

1. "Epitaxial Growth of B1 Structure NbN on Sapphire," J. R. Gavaler, J. Greggi, and J. Schreurs, Contributed talk given at March 1984 Meeting of the American Physical Society.

2. "High-T_c Superconducting Materials for Electronic Applications: Critical Issues," A. I. Braginski and J. Talvacchio, Invited Seminar at the MIT — Lincoln Laboratory, June 15, 1984 (also a meeting on cooperation under the AFOSR program).

(List interpersonal coupling with: Stanford U, U ~~Hot~~ Wisc-Mil, MIT-Lincoln Lab etc.)

8. PATENTS AND INVENTIONS

1. "A Method for Fabricating High-T_c Superconducting Tunnel Junctions," A. I. Braginski, Patent Disclosure RES 84-186.